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The Primary Decomposition Products of a Lignite Coal Upon Fractional Carbonization

THE PRIMARY DECOMPOSITION PRODUCTS OF A LIGNITE COAL UPON FRACTIONAL CARBONIZATION

BY

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THESIS

FOR THE

DEGREE OF BACHELOR OF SCIENCE

IN

CHEMISTRY

COLLEGE OF LIBERAL ARTS AND SCIENCES

UNIVERSITY OF ILLINOIS

1920

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June 7th 1920

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Acknowledgment

I wish to express my indebtedness to Dr. Layng, not only for his help, patience, and encouragement in this problem, but even more for creating a deeper appreciation of science and methods of research.

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THE PRIMARY DECOMPOSITION PRODUCTS OF A LIGNITE COAL UPON FRACTIONAL CARBONIZATION

I Introduction

1. Nature of the Problem. Knowledge of the original substances which have produced coal and of the conditions to which they were subjected is limited, for we know only the fossilized remains of the coal plants. Coal is generally considered, as expressed by V. B. Lewes, an agglomeration of the solid degredation products of vegetable decay, together with those original bodies which have resisted action (that is, resinous spores, etc.). Thiessen[1] says: "Coals are composed of a residue of the most resistant components of plants, of which resins, resin-waxes, and the higher fats and alcohols are the most important." He outlines the stages of coal information: (1) Death of the plants; (2) Partial decomposition and maceration, by fungi and bacteria. The most resistant components are left behind, forming peat. (3) The biochemical means change to dynamochemical ones. Lignite, the first coal formed during this stage is a residue of the most resistant plant structures and very resinous, the resins having suffered little change. The dynamochemical change is the least under-

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[1] Thiessen, R., "On the constitution and genesis of certain lignite and sub-bituminous coals." Original communication to the Eighth International Congress of Applied Chemistry, Vol. 25, pp. 203. 1912.

stood. Among the theories concerning it is the one stated by Lewes[2] that, starting with cellulose, the changes during the formation of coal can be explained by oxygenation, by infiltration of oxygen-carrying water, or by dehydration, the changes in the carbohydrates and extractives of the plants depending upon conditions. With moisture and air CO_2 and H_2O were formed, without air, CO_2 and CH_4. White[3] suggests: "The more powerful earth thrusts as the land rose and fell must have caused greater pressure, with resultant rise of temperature, ------bringing about a slow destructive distillation of the coal, gas relatively rich in oxygen being evolved, and the resultant coal remaining richer in carbon and poorer in hydrogen and oxygen."

A study of the compositions of different coals and of their formation is of value as a means of revealing the causal factors responsible for differences in their chemical and physical properties. Since lignites which, because of their moisture content, are difficult to burn and to ship, and are impossible to coke, make up the greater part of our coals, their composition is particularly interesting. Why are lignites

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[2] Lewes, V. B., "The Carbonization of Coal." Lectures before the Royal Society of Arts. Coal Age (abstract), March 9, 1912, p. 712.

[3] White, Park, and Dunkley, "Destructive distillation of coal at low temperatures," Journal of Gas Lighting, pp. 104, 348. 1908.

non-coking coals?

2. Historical. The reactions of coal are so susceptible to slight variations in conditions that it is difficult to compare the work of different investigators using different coal, methods, apparatus, and technique.

Porter and Ovitz[4] in 1908 compared the low temperature distillation products of different coals. The only work on lignite below 600° C. was done at a retort temperature of 580° C., yielding 8.2% of tar, 18.5% H_2O, and 1020 c.c. of gas per 100 grams of coal. Of the saturated hydrocarbons, about 75% was CH_4. No determination of O_2 is given, being assumed present only as air. In a later study[5] of the volatile matter of coal, 1910, they found that gases of western coals, usually considered the younger coals, contain more of the oxides of carbon, which are given off at low temperatures. But gas at temperatures as low as 300°-350° C. from any coal is rich in ethane and higher paraffins.

Burgess and Wheeler in 1910[6] distilled English coals at atmospheric pressure, using 2 gram samples. No lignite was included. Finding a larger per cent of the homologues of ethane below 400° C. and a large percent of hydrogen above

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[4] Porter and Ovitz, J. of Gas Lighting, pp.104,343. 1908.

[5] Porter and Ovitz, The Volatile Matter of Coal, Bulletin 1, Bureau of Mines. 1910.

[6] Burgess and Wheeler, J. C. S., pp. 97, 1917. 1910.

700° C., they conclude that coal contains two types of compounds: one, unstable, yielding C_nH_{2n+2} and no H_2; the other, decomposed with more difficulty and yielding H_2. In 1911[7] they state that the difference between coals is probably determined by the proportion in which these two types exist, and that the true "coal substance" is compounded of the two types which behave so differently under action of heat. At this time they introduced two-gram samples of coal into a preheated retort, keeping the temperature constant and taking samples of gas at short intervals. The luminants disappeared at higher temperatures, but these are not particularly considered, for they are not regarded as entering into the composition of "coal." The rate of formation of CO_2 was uniform, from which they supposed it due not to decomposition but to interaction of oxygenated compounds.

In 1914, Burgess and Wheeler[8] distilled 200 gram samples of bituminous coal in a vacuum. The occluded gases were first removed by evacuation at atmospheric temperatures, sometimes requiring several days. When the coal was first dried at 107° C., these gases were largely CO_2 and CO. With distillation at 200° C. there was copious water; at 310°, no marked increase in gas, but the appearance of oil; 350° was a decomposition point, marked by the evolution of much gas and oil; above 350° the CH_4 increased and the higher saturated hydrocarbons

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[7] Burgess and Wheeler, J. C. S., pp. 99, 650. 1911.

[8] Ibid., pp. 105, 131. 1914.

decreased.

M. Leo Vignon[9] in 1912 distilled 100-gram samples of Montrambert and gas coal in iron tubes held at the desired temperature until there was no further evolution of gas. He finds CH_4 liberated almost entirely below 600° C., no nitrogen below this point, and CO increasing with the temperature.

Parr and Olin (1912)[10] and (1915)[11] studied low temperature distillation products of Illinois coals to "discover some fundamental facts pertaining to the properties and characteristics of bituminous coals." They state three conditions influencing coking properties. (1) The presence of certain binding bodies with a definite melting point. (2) The decomposition point must be above this melting point. (3) The temperature of decomposition can be so lowered by oxidation as to alter the second condition.

Clark and Wheeler (1913)[12] conclude that the H_2 yielding and paraffin yielding substances are separate constituents

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[9] Vignon, L. M., (Fractional distillation of coal); Compt. rend., t. 155, 1912, pp. 1514-17; Jour. Soc. Chem. Ind., Vol. 32, p.76. 1913.

[10] Parr, S. W. and Olin, H. L., The Coking of Coal at Low Temperatures, U. of Ill. Eng. Exp. Sta. Bull. No. 60. 1912.

[11] Parr, S. W. and Olin, H. L., The Coking of Coal at Low Temperatures with Special Reference to the Properties and Composition of the Products, U. of Ill. Eng. Exp. Sta. Bull. No. 79. 1915.

[12] Clark and Wheeler, J. C. S., pp. 103, 1704. 1913.

of "coal," and that they can be separated by extractions with pyridine and chloroform.

Jones and Wheeler (1914)[13] and (1916)[14] regard "coal" as a conglomerate of cellulosic and resinic compounds. They assume the presence in "coal" of hydrogenated aromatic nuclei, which, they suggest, suffer decomposition, eliminating H_2, at temperatures not much below 400° C., while only the resinous substances in bituminous coals decompose to any great extent at temperatures below 500° C.

Pictet and Bouvier[15] in 1913 distilled 2 to 3 kilograms of coal at a pressure of a few centimeters of mercury, raising the temperature slowly to 450° C. Only the tar was studied. It equaled about 4% of the coal, was lighter than water, of a brown color, and contained no aromatics. The water contained no NH_3.

The thermal effects of carbonization were studied by Hollings and Cobb[16] who found that Cellulose has an exothermic reaction between 345° and 400° C. and that lignite shows something of the same effect.

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[13] Jones and Wheeler, J. C. S., pp. 105, 140. 1914.

[14] *Ibid.*, pp. 109, 707. 1916.

[15] Pictet, A., and Bouvier, M., (Distillation of Coal under reduced pressure): *Gas World*, Vol. 60, p. 45. 1914.

[16] Hollings, H., and Cobb, J. W., "Thermal study of the carbonization process," J. C. S. Vol. 107, p. 1106. 1915.

Babcock's[17] studies of the carbonization of lignite were confined to high temperatures only.

Taylor and Porter[18] investigated the primary volatile products from four types of American coals, including a Wyoming lignite, at 250°, 350°, 450°, and 600° C. A vacuum was used to pull off the gases as they formed and prevent secondary reactions. The duration of the test was about 13 hours, or during the principal evolution of volatile matter, about 1/2 hour sufficing to bring the 15 grams of coal used to the desired temperature. Some of the results were:

(1) The western coals (Illinois and Wyoming) yielded proportionately less tar and more water, decomposing more easily and evolving, at first, large amounts of CO_2.

(2) More than 2/3 of the organic substance of coal is decomposed at temperatures below 500° C., the first products being chiefly water, CO_2, and CO.

(3) With subbituminous coals volatile matter begins to distill in appreciable quantities below 250° C.

(4) The Wyoming type produced chiefly water and CO_2, rather than paraffins, at temperatures up to at least 450° C.

(5) Paraffin hydrocarbons of the series C_nH_{2n+2} higher than CH_4 predominate at temperatures below 400° C.

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[17] Babcock, E. J., Economic Methods of Utilizing Western Lignites, Bureau of Mines, Bull. No. 89. 1915.

[18] Taylor, G. B., and Porter, H. E., The Primary Volatile Products of the Carbonization of Coal, Bureau of Mines, Technical Paper 140. 1916.

(6) Water of decomposition is produced from coal at temperatures above about 250° C. but in greater amount below 500° C. than above.

In all of the work oxygen data in the analysis of gas is omitted.

Benson and Davis[19] in 1917 published results of low temperature distillation of a Washington lignite. Benson and Canfield[20] have recently published a continuation of the work. 1,000 grams were plunged into a heated retort; the temperature was kept constant and the pressure atmospheric for 24 hours. Gas was drawn out at intervals. The range of temperatures studied was from 150° to 600° C. In the tables recording their results the per cent of dry tar plus the per cent of aqueous solution is equal to the per cent of total distillate, the weight of the gas being disregarded. Results:

(1) At 200° C. there is no tar. The maximum yield, 5.4% is at 380° C. The specific gravity of the tar increases with the temperature from 0.975 to 1.033. It contains no benzol.

(2) The coke, or residue, between 250°--600° C., ranges from 63.8% to 48.8%.

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[19] Benson, H. K., and Davis, L. L., "Low temperature distillation of lignite coal," J. Ind. and Chem. Eng., Vol. 9, No. 10, pp. 946-949. 1917.

[20] Benson, H. K., and Canfield, R. E., "Low temperature distillation of sub-bituminous coal," J. Ind. and Chem. Eng., Vol. 12, No. 5, pp. 443-446. 1920.

(3) CO_2 between the same temperatures ranges from 82.4% -3.0%.

H_2 between the same temperatures ranges from 0.0% to 35%.

N between the same temperatures ranges from 33% to 14%. CO is high, 12% - 19%; O_2 is low and variable, about 1.5%.

(4) Appreciable amounts of NH_3 may be obtained from the tar water.

Summary of Historical Work. Little work on lignite has been done by the same investigator, excepting Taylor and Porter, and Benson and his co-workers, and the conditions and methods used by different workers are varied, many having omitted oxygen data, others analysed only the tars, etc.

Investigation of coals by means of solvents and low temperature distillation has, however, brought out the following facts. The products of any coal are hard to control because of the changes caused by occluded gases, oxidation, and moisture effects. They seem to be composed of two main types of compounds present in varying proportions,--"phenol soluble and phenol insoluble," "hydrogen yielding and methane yielding," etc. Some place between 300° and 400° C. there is a marked decomposition point, with evolution of oil, increase of CH_4, and decrease of higher members of the paraffin series. H_2 increases with the temperature.

Lignite is particularly susceptible to atmospheric conditions. It yields appreciable volatile matter below 250° C. Its low temperature products are rich in the oxides of carbon and in water.

3. *Purpose of present investigation*. The principal investigation has been an attempt to determine the primary volatile products of the carbonization of a lignite coal, with observations of any points at which marked decomposition of any particular type takes place. It is a part of a larger experiment carried on to determine the same products, under similar conditions, from four distinct types of coal.

But early in the course of the work it was decided to undertake some additional experiments on the effect of gases on coal, due to the following considerations:

Coke formation is dependent upon the presence of a luting body having a definite melting point which is also below the point of decomposition.[21] Professor Parr and H. F. Hadley also state, "In the case of lignites it is doubtless true that the absence of resinic bodies, or the oxidation to a large extent of such as they may have possessed, is the explanation for the lack of coking properties in such material." According to data recorded by these investigators lignite has a larger per cent of resinic matter, obtained with phenol as a solvent, than a West Virginia Pocohontas coal, indicating that the amount of phenol soluble matter is not the decisive factor.

That oxidation of coal impairs its coking properties is shown by the fact that coke is not obtained from otherwise coking coal after weathering or after heating at 107° C. for some time. But that this is not due to the oxidation of the

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[1] Parr, S. W. and Hadley, H. F., *The Analysis of Coal with Phenol as a Solvent*. Univ. of Ill. Eng. Exp. Sta. Bull. No. 76.

phenol soluble material is shown by two facts: (1) If the cellulosic residue of a coking coal is oxidized and added to the resinic extract, the mixture will not coke. (2) If the cellulosic residue is added to the oxidized resinic extract, coke can be obtained. If, however, before adding it to the phenol soluble matter, the oxidized residue is heated to 300° C. and evacuated, the mixture will coke. Are the coking properties then due to the nature of the cellulose?

The oxidation of coal causes an increase in the per cent of CO_2 in the gases of distillation. It is also known that both cellulose and total coal, particularly lignite, when distilled, first liberate CO_2. Is it not possible, then, that the CO_2 effects the resinic matter?

An explanation of these phenomena and the discovery of others necessary for their practical application calls for answers to such questions as: (1) Will CO_2 destroy the solvent effect of the luting body of coking coals? (2) Is there a connection between the fact that lignite yields large quantities of CO_2 and its inability to coke? (3) If CO_2 effects the resinic binder, what is the critical temperature, if there is one, at which it does so? (4) Can most of the CO_2 be liberated below this point?

II Experimental

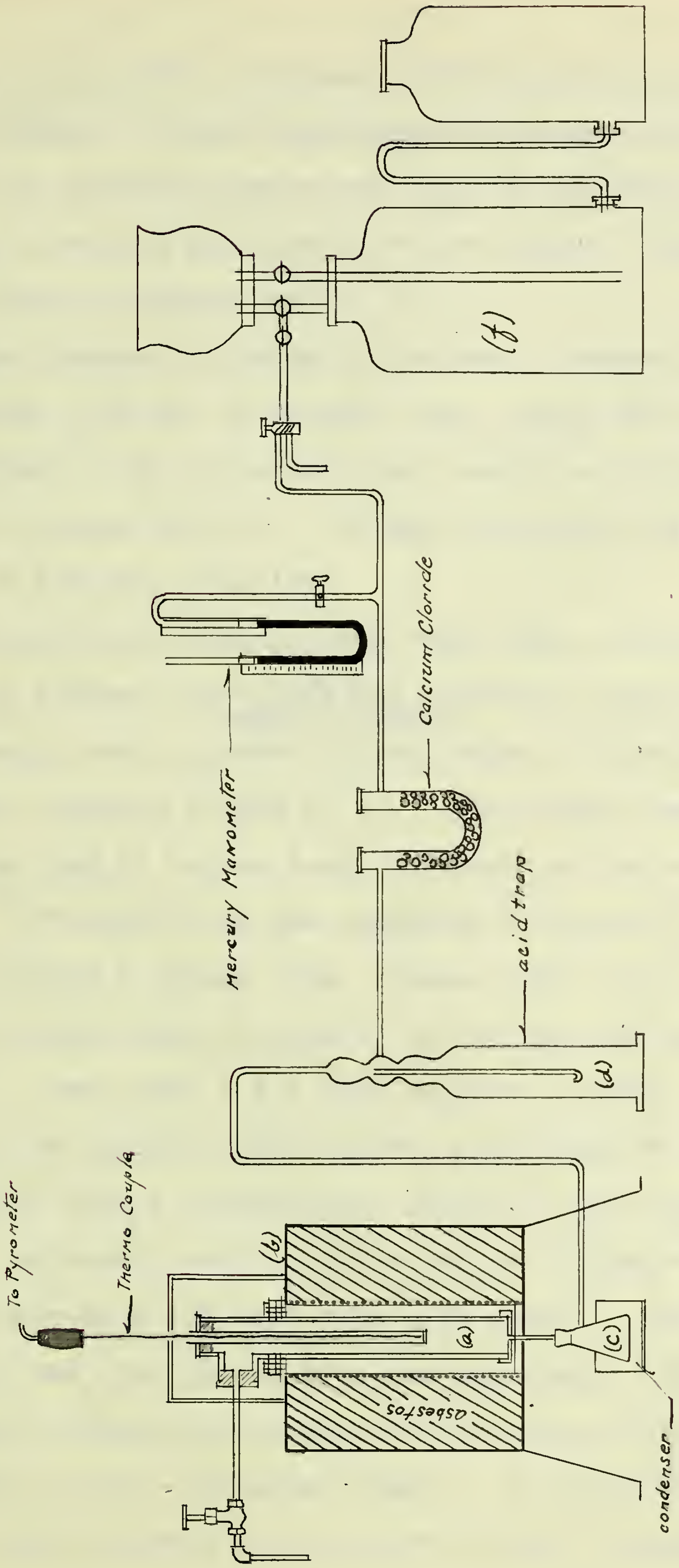
1. The Coal. The coal used was a lignite from Manitoba, Canada, which had been exposed to the air in the laboratory for twelve months. Two samples of it were air-dried, and ground to pass through a 60 mesh sieve. Sample A, with an air-drying loss of 12.9%, was ground in October and kept in a stoppered, glass container, being used for tests 1 to 15 inclusive, made from December to the following May. Sample B, with an air-drying loss of 10.6%, was ground in May and used within a few days for tests 16 to 19 inclusive.

Table I

Analyses of Coal Used in Experiments

	Sample A		Sample B	
	As received basis	Dry basis	As received basis	Dry basis
	per cent	per cent	per cent	per cent
Moisture	23.01	0.0	18.50	0.0
Volatile matter	31.55	41.00	34.00	41.70
Fixed carbon	37.03	48.10	39.89	48.96
Ash	8.41	10.90	7.61	9.34
Sulpher	0.54	0.70	0.56	0.69
Carbon	54.80	71.21	57.50	70.58
Hydrogen	4.61	5.98	4.94	6.06
Oxygen	16.21	21.03	17.63	21.60
Nitrogen	0.83	1.08	0.87	1.07

2. Apparatus. Considerable difficulty was experienced in securing an air tight apparatus that would stand the necessary heat. The form described, the most satisfactory one tried, was used for all of the tests after No. 6. Before that a pyrex glass retort, easily broken and hard to connect to the absorbtion train, was used. In its final form (Fig. 1) the apparatus con-


To Pyrometer
Thermo Couple
(b)
(a)
asbestos
(c)
condenser
(d)
acid trap
Calcium Cloride
Mercury Manometer
(f)

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sisted of an iron retort (a) placed vertically in an electric resistance furnace, (b), and connected at its lower end with a flask, (c), for condensing water and tar; an absorbtion flask, (d), for NH_3; a calcium chloride or sodium hydrate tube (e); and a large gas-collecting bottle, (f).

The furnace, 6 inches in internal diameter and 16 inches long, was wound with No. 14 chromel wire, lined with alundum cement, insulated with "silo-cel" and capable of giving a temperature of at least 850° C. It was controlled by an external resistance of 120 ohms capacity.

Temperature readings were taken from a millivoltmeter calibrated in degrees centigrade and connected with a thermocouple extending into a pocket in the center of the retort. Readings were accurate within 5° C. The retort was made from a 2 inch iron pipe 12 inches long, threaded on the outside, at both ends. The upper end was connected by means of a flange to a 2 inch nipple 3 inches long, screwed into a cap. An opening was drilled into the center of the cap and threaded from the inside. Into this a 1/2 inch pipe was screwed, extending down to half the length of the retort, and closed at the lower end by a cap to form a thermocouple pocket in the center of the coal mass. A second opening in the cap was threaded from the outside and carried a 1/4 inch pipe with valve. The lower end of the retort was also closed by a cap carrying a 1/8 inch pipe which extended through the bottom of the furnace into the rubber stopper of the condensing flask. An asbestos paper gasket was fitted between the two parts of the flange; graphite

ground in oil was used on all of the connections until higher temperatures were reached, when it was found necessary to weld most of the joints. An asbestos (or glass-wool at some of the lower temperatures) plug was put in the lower end of the retort to prevent the coal from falling through the gas outlet.

The greater part of the water and tar condensed in a filter flask connected, through the rubber stopper in its top, with the gas outlet pipe of the retort and to the NH_3 absorbtion bottle by means of the side arm. The connection here, like all others in the train, was made with a thick-walled rubber tubing just large enough to fit over the glass. This flask was cooled in running tap water or ice water. The NH_3 absorbtion bottle, containing a measured amount of acid, connected to a $CaCL_2$ U tube. Both were fitted with tight, ground glass stoppers. From the $CaCL_2$ the gas was led through a T tube connected to a mercury manometer and the tank. The latter was a 25 liter, glass tank into which the gas could be drawn or out of which it could be forced into the air by means of a two-way stopcock and a second leveling bottle. The gases were collected over salt water. A gas meter which could be read accurately to one thousandth of a cubic foot was used to measure the total gas and the nitrogen used to sweep out the apparatus after a run. This nitrogen, either obtained from a tank of nitrogen or made from NH_4CL and $NaNO_2$, was stored in an aspirating bottle, and was passed through concentrated sulphuric acid before entering the apparatus.

3. Operation. The air-dry coal was weighed before putting it in the retort, the flange tightened, and the whole immersed in water to test for leaks when filled with gas under a considerable pressure. The air tight retort was fixed in place in the furnace and connected with the train after which the entire apparatus was tested for leaks either by forcing in nitrogen to produce a pressure or by lowering the level of the water in the gas collecting outfit to cause a vacuum. A pressure of several inches of mercury could be maintained.

The apparatus was swept with nitrogen to expel air, the gas tank filled with water, and the furnace connected with the external resistance. The pressure was kept approximately atmospheric. The temperature was raised to the maximum as quickly as possible, requiring from 1/2 hour for the lower temperature to 1 1/2 hours for the higher, and maintained there during the principal evolution of gas. The duration of the average run was 3/4 hours. The system, after cooling over night, was swept with a measured volume of nitrogen and brought to atmospheric pressure, as gauged by the manometer, and the stopcock closed which imprisoned the gas in the tank.

The gas was metered, a sample being saved for analysis; the residue of coal was taken from the retort, weighed and placed at once in a tight jar; the water and tar were washed with a known amount of water into a separatory funnel; and the acid from the NH_3 absorbtion bottle was washed out and saved. The small amount of oil which had condensed on the surface of the acid was separated and added to the rest. The flasks were cleaned and

replaced for the next run.

4. Methods of Determination and Analysis of the Products.

Total volatile: The per cent of total volatile matter was calculated by subtracting from 100 the per cent of residue.

Total moisture: The water evolved was separated from the tar and run into a graduated cylinder. To it was added the acid and from this volume the known amount of acid and wash water was subtracted. Its specific gravity was considered 1.0 as it was found that this did not introduce a very large error. So much water is evolved from lignite that the amount absorbed by the $CaCL_2$ was comparatively negligible.

Water of decomposition has been calculated by subtracting from the total the moisture lost by oven drying at 110° C.

The NH_3 in the combined water and acid was determined by a Kjeldahl.

Tar: No attempt was made to dry the tar separated from the water. In most of the runs its specific gravity was determined in a picnometer bulb and used in calculating its weight. For those cases in which this determination was not made, an average value of 0.94 was assumed. The paraffins in the tar were determined by a Babcock fuming sulphuric acid test, and in some cases a concentrated sulphuric acid test for aromatics was made.

The gas was analysed, in a modified Orsat apparatus,

for CO_2, O_2, C_2H_4, C_6H_6, H_2, CO, CH_4, C_2H_6, and its higher homologues, and N_2 by difference. These results were calculated to a basis including NH_3 and excluding added N_2. The volume of each constituent and its total weight has been calculated per 100 grams of coal.

Residue: The moisture and ash content was determined in the usual way. As indicated in the results, however, when some of the residues were dried at 110° C. in an atmosphere of CO_2, there was a slight gain rather than loss in weight. All attempts to analyse for volatile matter failed. In platinum crucibles with fairly tightly fitting covers it was impossible to prevent mechanical loss even after saturating with kerosene and heating very slowly.

5. Experiment to Determine Duration of Evolution. In tests No. 1 and No. 4 the temperature was held at a maximum for 6 1/2 and 2 hours respectively, and the rate of evolution of gas noted.

6. Determination of Gas Evolved at Room Temperature. In testing the apparatus for leaks preparatory to making a run, it was noticed that a pressure could be easily maintained in the system but that a vacuum was sometimes quickly changed to atmospheric or even a more than atmospheric pressure. A sample of gas taken while sweeping the apparatus with N_2, analysed almost 50% CO_2. To determine whether the coal at room temperature (24° C.) was giving off gas, the system was connected with a gas receiving bottle at a vacuum of 16 1/2 inches of water for 2 hours.

7. Outline of the Experiments on the Effect of Gases on Coal.

The following tests were made:

(a) Test Run No. 153. Determination of the effect of CO_2 on the coking properties of a coking coal. Pulverized Franklin County, Illinois, coal was heated between 300° and 400° C. in an atmosphere of CO_2 and then the temperature was quickly raised to 740° C.

(b) Test Run No. 154. Attempt to remove CO_2 from lignite with lime and add H_2 gas. 400 grams of lignite ground to 60 mesh for 4 months and 20% added lime were heated to 640° in an atmosphere of H_2.

(c) Test Run No. 156. Attempt to determine whether CO_2 can be removed from lignite at 300° C. by use of vacuum, and leave the resinic matter uneffected. The method was to heat the coal at 300° until most of the gas was evolved and to then apply heat strongly.

(d) Test Run No. 158. Effect of carbonizing lignite plus 20% pitch.

III Presentation and Discussion of Results

I. Duration of Evolution of Gas. Within 15 minutes after the maximum temperature was reached in Test No. 1, the rate of evolution of gas began to decrease and continued to do so noticeably during the slight increase until the test was ended four hours later. When the maximum temperature was reached in Test No. 4, the evolution of gas through the acid bottle was at the rate of 90 bubbles per minute and was followed by a steady decrease to 18 bubbles per minute at the end of 1 1/4 hours. This rate was almost constant until the end of the run 1 hour later.

From these results it seemed impracticable to continue the remaining tests until the absolute cessation of gas evolution. In all of the tests it was noticed that the principal evolution was during the first 15 minutes after the temperature was reached.

2. Evolution of Gas at Room Temperature. In two hours 300 grams of coal at 24° C. delivered about 150 c.c. of gas containing 14% of CO_2 and 6.5% of O_2.

3. Effect of Gases on the Coking Properties of Coal. Test run No. 153. Heated in at atmosphere of CO_2, Franklin County coal yielded a residue which appeared to be amorphous carbon.

Test run No. 154. The addition of 5% lime has no apparent effect upon the delivery of CO_2 from lignite. Since the highest temperature used (640° C.) is far below the decomposition point of $CaCO_3$, it does not seem probable that the CaO could have acted as a catalyser.

Test run No. 156. The use of a vacuum at 300° C. does not remove all of the CO_2 from lignite and does not effect its coking properties.

Test run No. 158. The greater part of the charge of lignite plus 20% pitch did not coke, but the bottom three inches was removed in one piece and showed coke structure.

4. Results of Fractional Carbonization. The results of distillation of the lignite at different temperatures are presented in tables II, III, and IV. Analyses of the tars and cokes are given in tables V and VI, respectively. In the graphs the yields of products have been plotted against the temperatures. It is perhaps significant that few of these points fall on a smooth curve and that even duplicate runs of the same temperatures do not check. In general the curve has been drawn through the average points with exceptions when these seemed to be obviously incorrect. The results for total volatile matter, in particular, follow no curve and no attempt has been made to connect these points. (Fig. II.)

There are criticisms of the technique which would account for some of these variations but they do not offer an adequate explanation of them all. Of course a uniform sample of any substance treated in exactly the same way must, necessarily, react the same, but lignite seems to be too susceptible to slight changes in conditions, and particularly, atmospheric conditions, to obtain checking results without the use of much more delicate methods. A variable factor in the first tests was the duration. In tests No. 5 and No. 6, No. 1 and No. 4, and No. 8 and No. 9,

Table II

Products of Heating Coal at Successive Temperatures in Per Cent of Coal[1]

Test No.	Temp. °C.	Pressure Inches Mercury	Duration Hours	Duration Max. Temp. Hours	Total Volatile Matter per cent	Moisture not of Decomposition	Water of Decomposition	Tar (not dry)	Gas
5	260	vacuum 1½-⅝	11½	5	17.21	11.60		0.0	4.61
6	260	vacuum 1½-¾	7¾	3		11.60		0.0	2.89
1	310	3¼	9½	5	13.80	11.60	0.33	0.0	4.07
4	310	¾-3⅝	6	2	17.50	11.60		0.0	3.50
8[2]	360	Slight	4		35.70	11.60	16.10	2.14	7.52
9	360	Slight	2	1+	26.40	11.60	22.40	2.38	5.72
10	405	Slight	3	1	37.40	11.60	11.00	4.45	10.05
11	405	Slight	3	1½	34.30	11.60	11.30	5.62	6.95
12	450	Slight	3½	1	27.40	11.60	12.00	5.55	14.95
13	455	Slight	4	1¼	39.30	11.60		4.15	10.89
14	500	Slight	4¼	1½	40.60	11.60	9.70	3.88	10.65
15	500	Slight	3	1	40.8	11.60	12.40		13.52
16[3]	550	Slight	3¼	1	34.2	8.83	10.00	5.50	15.85
17	550	Slight	3½	1	30.80	8.83	18.82	5.78	14.47
18	600	Slight	3	1¼	35.70	8.83	15.37	3.96	23.20
19	600	Slight	3½	1¼	35.90	8.83		3.71	20.22

[1] All per cents are tabulated on the as-received basis.

[2] Began use of iron retort at this point.

[3] Following runs were made on Sample B.

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Table III

Products of Heating Coal at Successive Temperatures

Gas in c.c. per 100 grams cool

Test No.	Temp. ° C.	Total Gas	CO_2	O_2	C_2H_4	C_6H_6	H_2	CO	C_2H_6	CH_4	NH_3	N_2
5	260	3595.0	427.0	489.2	0.0	43.2	21.5	36.1				2578.0
6	260	2205.0	496.0	279.5	0.0	0.0	55.3	66.2	0.0	0.0		1308.0
1	310	3090.0	828.0	342.5	6.1	0.0	123.6	99.8	0.0	0.0		1690.0
4	310	2515.0	856.2	85.5	30.2	20.1	45.4	80.6	0.0	0.0		1397.0
8	360	5455.2	2694.0	136.2	32.8	132.0	872.5	360.0	677.0	92.7		458.0
9	360	4596.0	1647.0	128.7	119.5	64.0	694.0	307.7	716.5	358.2	27.6	532.5
10	405	8377.8	3001.0	251.4	159.0	150.8	1148.0	745.1	67.0	1013.5	654.0	1188.0
11	405	7633.2	3796.3	53.5	106.0	124.5	909.1	565.0	810.0	275.5		992.5
12	450	11640.2	4842.3	279.1	139.0	174.5	1746.7	640.0	1151.1	690.0	174.5	1803.0
13	455	8576.1	3361.8	128.8	94.5	128.8	1466.0	781.8	967.0	437.6	137.3	1072.5
14	500	9746.2	3801.0	156.0	185.1	48.7	2364.0	487.5	507.0	1686.0		510.9
15	500	11496.0	4104.1	172.4	149.3	115.9	2119.0	838.0	930.0	1287.3		1780.0
16	550	16379.8	5503.6	147.3	114.5	163.8	5929.5	507.5	458.0	1443.1	327.5	1785.0
17	550	15208.9	3969.5	166.9	212.9	137.0	4777.6	760.0	1004.0	1852.0	381.0	1948.0
18	600	21325.1	5672.5	362.1	192.0	980.9	6226.9	1456.2	2067.0	1470.0	447.5	2450.0
19	600	19198.9	5260.5	480.0	172.7	172.7	4955.1	1919.9	2148.0	1036.0	384.0	2670.0

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Table IV

Products of Heating Coal at Successive Temperatures

Composition of gas in per cent

Test No.	Temp. ° C.	CO_2	O_2	C_2H_4	C_6H_6	H_2	CO	C_2H_6	CH_4	NH_3	N_2	% of C_nH_{2n+2} Higher Than CH_4
5	260	11.8	13.7	0.0	1.2	0.6	1.0				71.7	
6	260	22.5	12.7	0.0	0.0	2.5	3.0	0.0	0.0		59.3	
1	310	26.8	11.1	0.2	0.0	4.0	3.2	0.0	0.0		54.7	
4	310	34.0	3.4	1.2	0.8	1.8	3.2	0.0	0.0		55.6	
8	360	49.4	2.5	0.6	2.4	16.0	6.6	12.4	1.7		8.4	88
9	360	35.8	2.8	2.6	1.4	15.1	6.7	15.6	7.8	0.6	11.6	65
10	405	35.8	3.0	1.9	1.8	13.7	8.9	0.8	12.1	7.8	14.2	61
11	405	49.8	0.7	1.4	1.6	11.9	7.4	10.6	3.6		13.0	75
12	450	41.6	2.4	1.2	1.5	15.0	5.5	9.9	5.9	1.5	15.5	62
13	455	39.2	1.5	1.1	1.5	17.1	9.1	11.3	5.1	1.6	12.5	89
14	500	39.0	1.6	1.9	0.5	24.3	5.0	5.2	17.3		5.2	23
15	500	35.7	1.5	1.3	1.0	18.4	7.3	8.1	11.2		15.5	42
16	550	33.6	0.9	0.7	1.0	36.2	3.1	2.8	8.8	2.0	10.9	24
17	550	26.1	1.1	1.4	0.9	31.4	5.0	6.6	12.2	2.5	12.8	35
18	600	26.6	1.7	0.9	4.6	29.2	6.8	9.7	6.9	2.1	11.5	58
19	600	27.4	2.5	0.9	0.9	25.8	10.0	11.2	5.4	2.0	13.9	67

Table V

Yield and Composition of Tar

No. of Test	Temperature Degrees C.	Wet Tar Per Cent	Paraffins Per Cent	Aromatics Per Cent	Unsaturated Hydro-carbons Per Cent	Specific Gravity
5	260	0.0				
6	260	0.0				
1	310	0.0				
4	310	0.0				
8	360	2.14				
9	360	2.38	8			0.932
10	405	4.45	30			0.901
11[1]	405	5.62	See Footnote			0.983
12	450	5.55	10			
13	455	4.15				
14	500	3.88	10			0.935
15	500	6.20	8	2	90	0.969
16	550	5.50				
17	550	5.78	10	14	76	
18	600	3.96	10			
19	600	3.71	24	8	68	

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[1] Per cent paraffins + aromatics = 20%

Table VI

Yield and Composition of Residue

Number of Test	Temperature Degrees C.	Residue Per Cent	Moisture Per Cent	Ash Per Cent
5	260		5.31	9.91
1	310	86.2	2.67	10.72
4	310	82.5	5.15	10.74
8	360	64.3	0.60*	13.13
9	360	73.6	0.01	13.73
10	405	73.6	1.69	13.56
11	405	65.7	0.47	14.39
12	450	72.6	0.35	14.84
13	455	60.7	0.03*	14.56
14	500	59.4	0.74	15.55
15	500	59.2		
16	550	65.8	0.33	13.65
17	550	69.2	0.29	14.41
18	600	64,3	0.14*	13.63
19	600	64.1	0.25*	13.64

*Gained in oven.

[illegible]

[illegible]

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
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		[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

[illegible]

[illegible]

Fig. II.

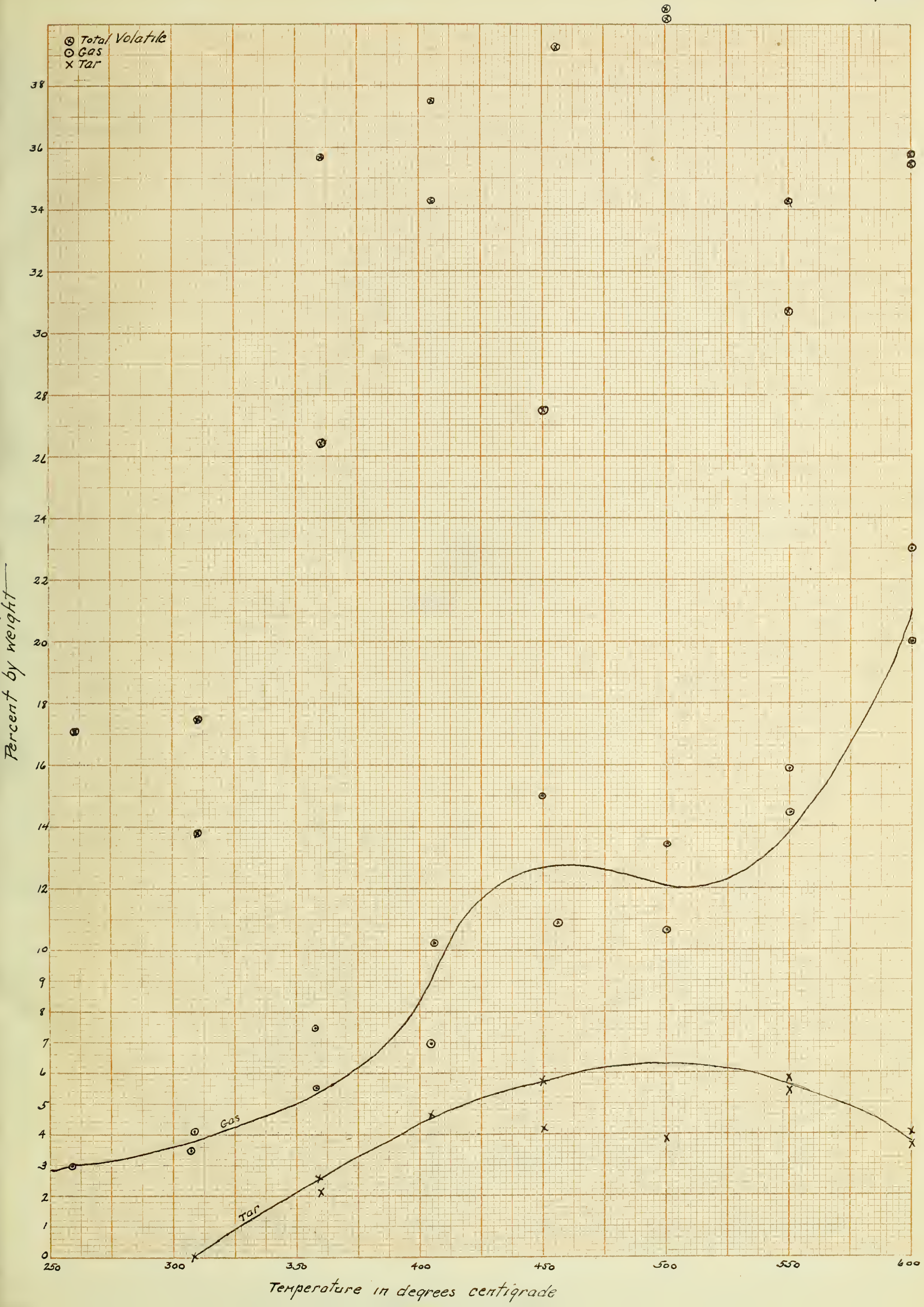
⊗ Total Volatile
⊙ Gas
× Tar
38
36
34
32
30
28
26
24
22
20
18
16
14
12
10
9
8
7
6
5
4
3
2
1
0
Percent by weight
Gas
Tar
250
300
350
400
450
500
550
600
Temperature in degrees centigrade

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Fig. III.

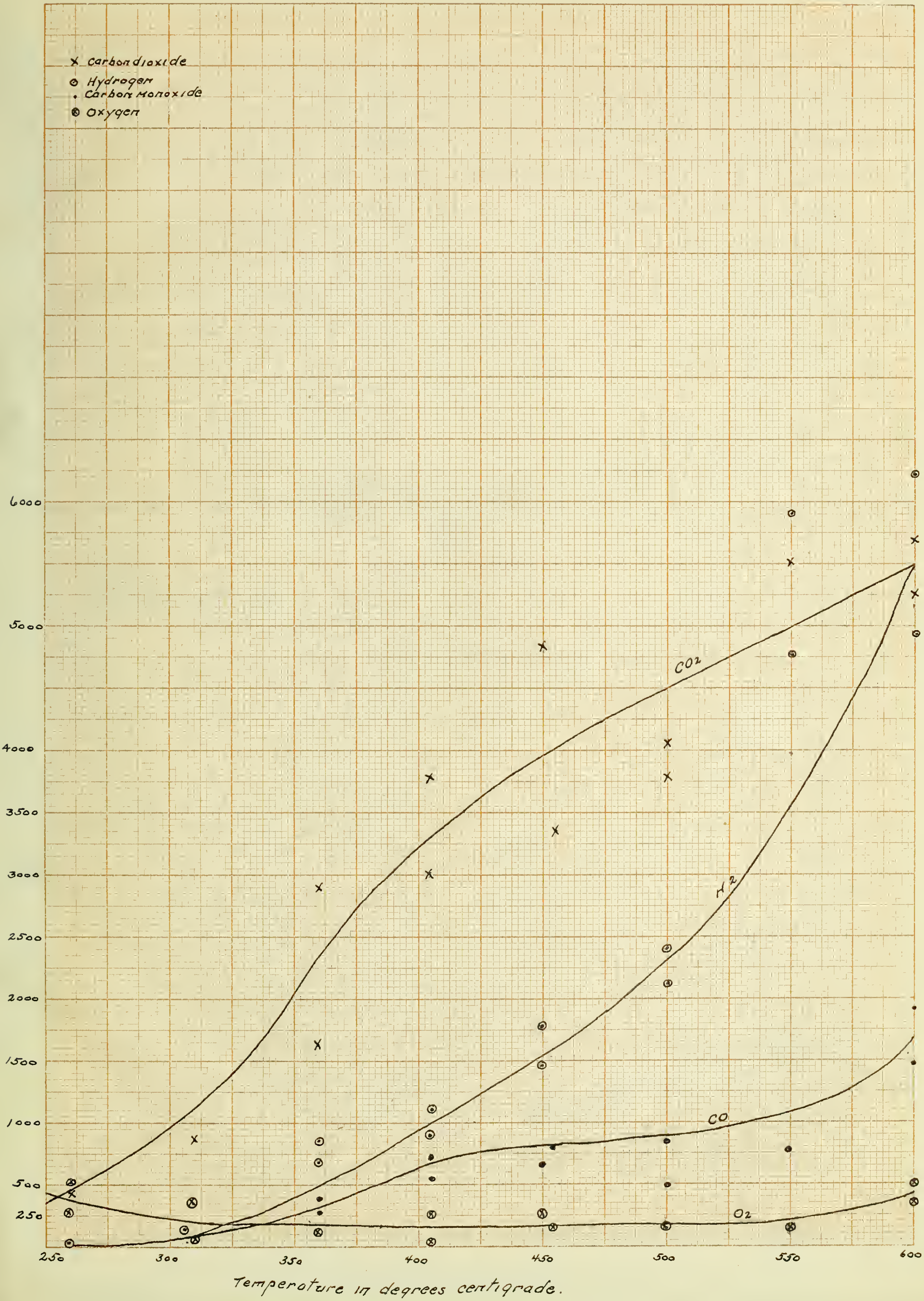
× Carbondioxide
⊙ Hydrogen
• Carbon Monoxide
⊗ Oxygen
6000
5000
4000
3500
3000
2500
2000
1500
1000
500
250
250
300
350
400
450
500
550
600
CO2
H2
CO
O2
Temperature in degrees centigrade.

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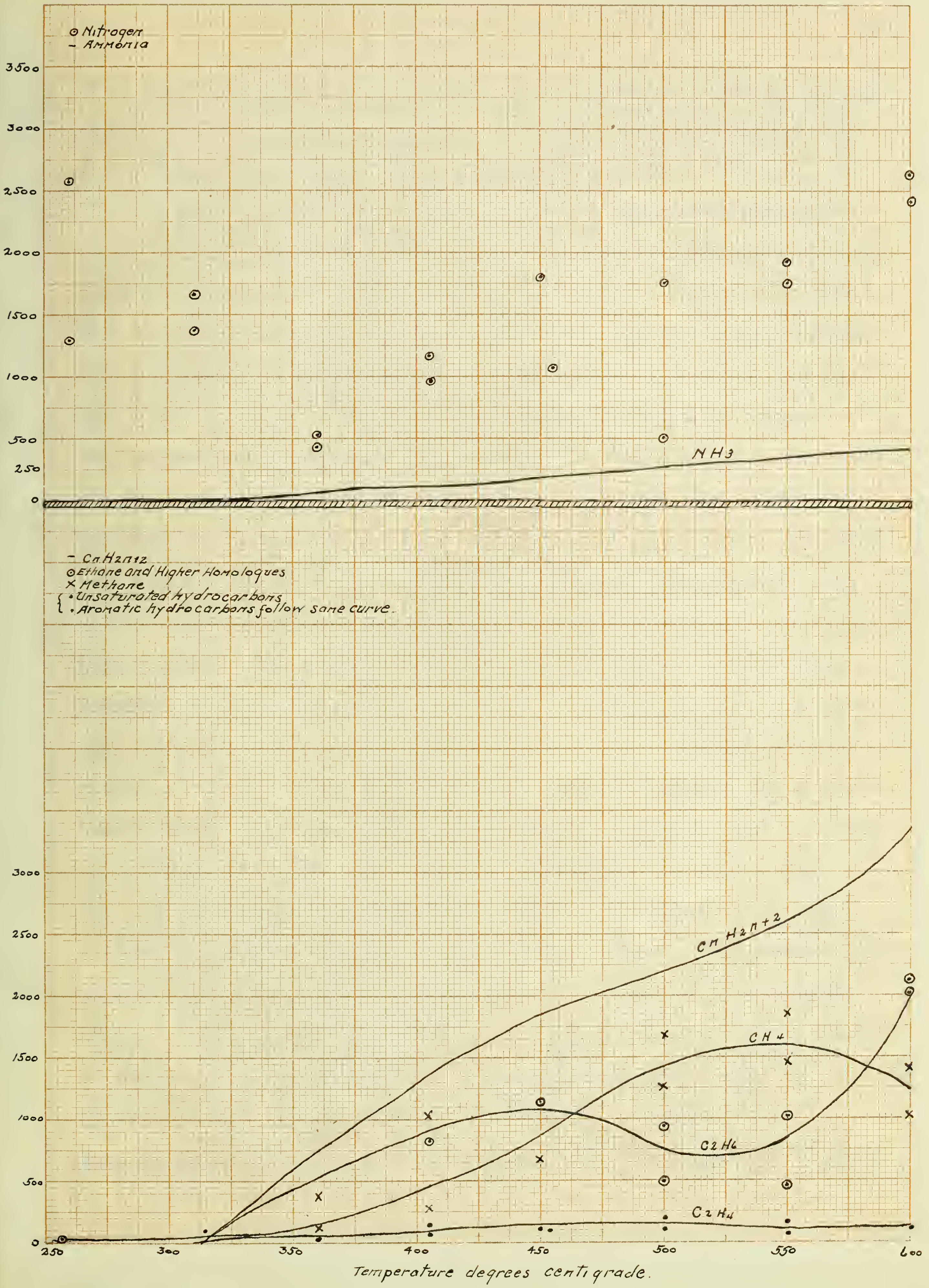
Fig. IV.


⊙ Nitrogen
- Ammonia
3500
3000
2500
2000
1500
1000
500
250
0
NH3
- CnH2n+2
⊙ Ethane and Higher Homologues
× Methane
• Unsaturated hydrocarbons
• Aromatic hydrocarbons follow same curve.
3000
2500
2000
1500
1000
500
0
Cn H2n+2
CH4
C2H6
C2H4
250
300
350
400
450
500
550
600
Temperature degrees centigrade.

this seems to have had its effect in the amounts of total volatile matter and total gas delivered. But this does not account for the greater evolution in No. 6 (the shorter run) of CO_2, H_2, and CO than was found in No. 5, and in some of the other cases, particularly No. 10 and No. 11, the results are the opposite of what would be expected. But they show that for a strict comparison the duration should be for a definite time and not simply during the principal evolution of gas. The method of cooling the system after a run introduced another possible source of error. The hygroscopic coke was left to cool in connection with the rest of the train. This might have changed not only the weight of residue, and thus the per cent of total volatile matter, but also the composition of the products by their absorbtion back into coke. The residue should have been removed and cooled in tight containers. The results for water of decomposition are inconsistent, making the sum of per cents of total moisture, tar, and gas, in some cases, greater than the per cent of total volatile matter. In all cases the charge of coal was weighed and transfered to and from the retort as quickly as possible, but it takes up moisture so easily in moist air, releasing it in dry, that the moisture content is hard to control. In weighing up small samples it gains rapidly on the balance. Some of the differences, however, are too marked to be within the limits of experimental error, as any of the curves show. Perhaps, however, the sample is not perfectly homogeneous. In his microscopic study, Dr. Thiessen finds coals, particularly lignites, composed of a heterogeneous mixture of parts of many different kinds of plants

in various stages of degradation. Those parts consisting chiefly of the products of the resins of the plants contain "resins, resin waxes, waxes, and higher fats, or the derivatives of the compounds composing these." Unless, then, it were possible to divide these microscopic constituents by very fine methods of grinding, we could not expect their distribution to be entirely uniform, and the distribution should have its effect on the products. For example, an alcohol close to a fatty acid might be expected to deliver compounds different from those of two fatty acids.

But the results follow sufficiently well defined rules to bring out the following noticeable features: (1) In duplicate runs, oxygen generally decreases when CO_2 and CO increase, or when hydrogen decreases, indicating that the oxygen of the coal may be liberated in varying proportions of carbon dioxide, carbon monoxide, and water, due, perhaps, to variations in temperature control. (2) The volumes of oxygen, carbon monoxide, and hydrogen increase with the temperature. Fig. III. (3) Nitrogen and ammonia also increase. (4) The per cent of carbon dioxide decreases. Fig. III. (5) There seems to be a decomposition point marked by simultaneous appearance of tar and increase in evolution of gas, at 300°-360° C. Fig. II. C_nH_{2n+2} is first found in the gas at this point. (6) As total C_nH_{2n+2} increases ethane decreases (except for a final rise at 600° C.) and methane increases. Fig. IV. (7) Unsaturated hydrocarbons increase gradually with the temperature. Fig. IV.

In an attempt to explain the results the constitution of the material distilled must be considered. Coal may be

separated by phenol as a solvent into two products which are called cellulosic and resinic for want of better names. The resinic material is made up of fatty acids, alcohols, esters, and the hydrocarbon degradation products of these, namely aliphatic, acyclic, and aromatic hydrocarbons. Coal has the ability, also, to adsorb any gas with which it is in contact. We may, therefore, say that coal contains uncombined O_2, N_2, the products noted above, and small amounts of any of the gases formed in the degradation of these products.

We should then be able to account for the results of destructive distillation by consideration of the thermal reaction of the above constituents. These will be of two kinds, first, destructive decomposition of the coal itself and inter-reactions of its products, and secondly,the effects of previously occluded gases after their liberation by increased temperature. By occluded or adsorbed gases are meant, in this discussion, those which are at some time taken up by the coal and later liberated unchanged. These latter effects would not be expected to continue long; they would include the evolution of the unchanged gases, and the oxidation of the coal by some of the oxygen. Such an oxidation need not necessarily be of carbon, but would more probably be of some such type as the readier oxidation of alcohols to acids accompanied by the splitting off of water.

Decomposition of fatty acids first begins, probably, by formation of the anhydrides of the acids followed by formation of ketones and loss of carbon dioxide. In this connection, it

was noticed from the data that water and carbon dioxide are the first principal products of distillation.

If, at this stage, the ketone is oxidized, more water and lower fatty acids will result, followed by a repetition of the reactions. But oxidation affects would not be expected to continue long, and the products should become more and more those of destructive distillation. Decomposition of the ketones and fatty acids without oxidation would result in the production of methane and ethane, which are observed, in the data, to be the next gases liberated.

It is notable both in this and in other investigations that as the volume of total gases of the series C_nH_{2n+2} increases, the higher members decrease, while the methane and unsaturated hydrocarbons increase. This is easily explained when it is considered that paraffins decompose by the following stages: $C_nH_{2n+2} \longrightarrow C_nH_{2n} \longrightarrow C_nH_{2n-2} \longrightarrow C_nH_n \longrightarrow C_nH_{n-2} \longrightarrow C + H$.

Cyclic compounds are more stable. Those of low molecular weight would be expelled at lower temperatures. If quite large, they may be retained until a temperature sufficient to break the ring is reached when the resulting aliphatic compounds would decompose to unsaturated molecules. On the other hand, aliphatic compounds, losing some of their hydrogen atoms and side chains would condense to ring structures which, if small enough, would go into the gas at low temperatures but which, if of higher molecular weight would not be expelled or broken down until later.

Due to carbon's great affinity for carbon, the total

effect is, then, one of carbonization, condensing the carbon into more and more stable structures of itself (which may be either large, stable molecules, or simply masses of attracted, small molecules) and splitting off those groups for which it has less affinity. (C_2H_5), (CH_3), (C_6H_5), and (OH) groups would be split off with hydrogen. And compounds of the type of benzene would condense with loss of hydrogen to form naphthalene, anthracene, etc., accounting for the increase of hydrogen at high temperatures.

Then if the temperature is increased or even, probably, if the time of distillation without raising the temperature is increased, the oxygen evolved from the coal itself, will have less and less opportunity of combining with carbon, due to carbon's greater, and increasing tendency to combine with itself. Such a theory would explain the decrease in the per cent of carbon dioxide and the increase in free oxygen as distillation progresses.

Some of the reasons for attributing to carbon a greater affinity for itself than for other elements are the facts that it is the only element which forms compounds consisting of long chains of itself and that it is hard to oxidize. There are many indications of this difficulty of oxidation: (1) Carbon adsorbs oxygen which it expels at higher temperatures as free oxygen, not as carbon dioxide. (2) Pure carbon has a very high kindling temperature. Even coke with a large per cent of fixed carbon and little volatile matter requires a force draft to burn.

Oxygen from the coal will not combine with hydrogen either, unless it is split off in some form in which one of its

valences is already combined, as in a hydroxyl group, for hydrogen, too, has a high kindling temperature.

Even if carbon dioxide is formed at higher temperatures as the result of decomposition of acids, it would tend to dissociate again since the reactions $CO_2 \longrightarrow CO+O$, and $CO \longrightarrow C+O$ are endothermic.

IV Summary and Conclusions

I. It is difficult to obtain the same products from two samples of lignite at the same temperature, not only because of its susceptibility to slight changes in conditions and the fact that it gives off appreciable amounts of gas at even room temperatures, but also, probably, because of the non-homogeneous nature of the coal itself.

2. It seems probable that there is a connection between the fact that lignite yields large quantities of carbon dioxide upon carbonization and the destruction, by carbon dioxide, of the solvent effect of the luting bodies of a coking coal. Whether or not this occurs at some definite point was not ascertained, but there seems to be a well defined point of decomposition of the resinous matter between 300° and 350° C. when tar and heavy fumes first appear. Lignite can not be freed of carbon dioxide below this point by use of a vacuum.

3. The change in composition of the gases at successive temperatures is according to the following general rules:

The volumes of oxygen, carbon monoxide, hydrogen, nitrogen, and ammonia are increased with the temperature.

The per cent of corbon dioxide decreases with the temperature.

Hydrocarbons of the series C_nH_{2n+2} are first found in the gases between 300° and 360° C. As the total volume of this series increases, ethane and the higher members decrease, while methane increases.

Unsaturated hydrocarbons increase gradually as the temperature is raised.

4. To explain these phenomena it is suggested that the effect of carbonization is to split off from the many types of carbon compounds composing coal those elements, radicals, and side chains which have less affinity for carbon than carbon has for itself, and to leave the carbon condensed into increasingly more stable structures of itself, thus lessening the per cent of carbon compounds which will be liberated as the temperature or the time of distillation is increased.

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